Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications

Xianliang Zhou, Honglian Gao, Yi He, and Gu Huang
Wadsworth Center, New York State Department of Health, Albany, New York, USA

School of Public Health, State University of New York at Albany, Albany, New York, USA

Steven B. Bertman
Department of Chemistry, Western Michigan University, Kalamazoo, Michigan, USA

Kevin Civerolo
New York State Department of Environmental Conservation, Albany, New York, USA

James Schwab
Atmospheric Sciences Research Center, State University of New York at Albany, Albany, New York, USA

Received 12 September 2003; revised 23 October 2003; accepted 10 November 2003; published 11 December 2003.

[1] Nitric acid (HNO_3) is the dominant end product of NO_x (= NO + NO_2) oxidation in the troposphere, and its dry deposition is considered to be a major removal pathway for the atmospheric reactive nitrogen. Here we present both field and laboratory results to demonstrate that HNO_3 deposited on ground and vegetation surfaces may undergo effective photolysis to form HONO and NO_x, 1–2 orders of magnitude faster than in the gas phase and aqueous phase. With this enhanced rate, HNO_3 photolysis on surfaces may significantly impact the chemistry of the overlying atmospheric boundary layer in remote low-NO_x regions via the emission of HONO as a radical precursor and the recycling of HNO_3 deposited on ground surfaces back to NO_x. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Zhou, X., H. Gao, Y. He, G. Huang, S. B. Bertman, K. Civerolo, and J. Schwab, Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications, *Geophys. Res. Lett.*, *30*(23), 2217, doi:10.1029/2003GL018620, 2003.

1. Introduction

[2] Several recent atmospheric field measurements at low-NO_x rural sites showed unexpectedly high daytime HONO concentrations during the summer season (Table 1), with average boundary layer noontime mean concentrations in the range of 53–110 pptv (parts per trillion by volume). Photolysis of HONO at these ambient concentrations, at a rate of about 200–400 pptv hr^{-1}, contributed between 20% and 40% to the overall radical budget in these rural environments. This source has typically been ignored in urban and regional photochemical models. To maintain the observed concentrations against its effective photolysis (~15 min lifetime), a strong HONO source must exist, 1–2 orders of magnitude greater than that from NO + OH reaction and from the dark HONO formation mechanism, mainly from heterogeneous NO_x-H_2O reactions, calculated from nighttime HONO accumulation [*Zhou et al.*, 2002a]. We hypothesize that HNO_3 photolysis on ground surfaces is the missing HONO source. As is well known, HNO_3 is a highly "sticky" species and its deposition to the ground surface is an important pathway for removal of total reactive oxidized nitrogen (NO_y) from the atmosphere [*Finlayson-Pitts and Pitts*, 2000]. HNO_3 accumulates on ground surfaces, including vegetation, in the absence of precipitation. When exposed to sunlight, the HNO_3 undergoes photolysis and produces HONO as one of the products, in the presence of water vapor. This proposed daytime HONO formation mechanism is supported by field observations of significant photochemical production of HONO in snowpack during the Polar Sunrise Experiment 2000 in Alert (Alert'2000) [*Zhou et al.*, 2001] and in a sunlight-exposed glass sample manifold during the PROPHET 2000 summer intensive in Pellston, MI [*Zhou et al.*, 2002b].

2. Experimental

[3] To investigate HONO production from surface HNO_3 photolysis, a series of laboratory experiments were carried out. A 7-turn glass coil flow reactor was used, which was made from 2-cm OD and 1.6-cm ID Pyrex tubing with an inner helix diameter of 20 cm, with a total volume of about 1 L and a surface area of about 0.4 m^2. The inner wall-surface was first coated with HNO_3 using a HNO_3 permeation source (VICI) at a gas-phase concentration of about 1–6 ppbv (parts per billion by volume) for at least 12 hours. Coating efficiency was monitored in some experiments by measuring HNO_3 concentrations in the airflow entering and exiting the reactor, using a measurement technique of *Huang et al.* [2002]. At a HNO_3 concentration of about 5 ppbv, a flow rate of 1.5 L min^{-1} and a relative humidity (RH) of 50%, gaseous HNO_3 was quantitatively adsorbed onto the wall surface of the reactor at the beginning of the

Copyright 2003 by the American Geophysical Union.
0094-8276/03/2003GL018620

Table 1. Noontime HONO Concentrations and Photolysis Rates at Low-NO_x Rural Ground Sites (Average $NO_x \leq 1000$ pptv)[a]

Site & date	Noontime HONO, pptv	Photolysis rate, pptv hr^{-1}
Pinnacle State Park, NY, summer 1998[b]	60	230
Summit, Whiteface Mountain, NY, summer, 1999	55	220
UMBS, Pellston, MI, summer, 2000[c]	53	210
Lodge site, Whiteface Mountain, NY, summer, 2002	110	425

[a]Photolysis rate constants were computed using actinic flux values, absorption cross section, and quantum yield obtained from *Finlayson-Pitts and Pitts* [2000] and references therein. The photolysis rate constants were corrected for the variable cloud coverage using the Eppley radiometer measurements following the method of *Kleinman et al.* [1995].
[b]From *Zhou et al.* [2002a].
[c]The HONO concentration was measured within the canopy level.

coating process. It took about 3 hours for 90% of the gaseous HNO_3 to pass through the reactor unretained. During the photochemical experiments, high-purity zero air was passed through the reactor at a flow rate of 1.5–3.5 L min^{-1} with the RH adjusted between 0 and 80%. To counter possible surface HNO_3 photolytic loss, 1–2 ppbv of HNO_3 was added to the zero air entering the reactor. No difference in photoproduction signals was observed with or without the added gas-phase HNO_3. The adsorbed HNO_3 was rinsed off the reactor inner wall surface with 100 mL deionized water and analyzed immediately [*Huang et al.*, 2002]. A 400-W medium-pressure mercury lamp (Ace Glass) was placed in the center of the helix. The light source was filtered with a Pyrex sleeve (UV-cutoff wavelength 290 nm) to remove low-wavelength UV light and a quartz well filled with circulated water to remove heat-generating IR light. Effective UV intensity was monitored using a nitrate actinometer [*Jankowski et al.*, 1999]. All the data reported here have been normalized to the tropical noontime condition with an aqueous nitrate photolysis rate of 3.0×10^{-7} s^{-1} [*Jankowski et al.*, 1999]. HONO production rates were determined by monitoring the concentrations in the air flow immediately before and after the flow reactor, using a measurement technique based on coil scrubbing/azo dye derivatization/HPLC analysis [*Huang et al.*, 2002]. The detection limit of the technique is better than 5 pptv. A chemiluminescence NO_x analyzer (TEI, Model 42C Trace Level) with a photolytic NO_2 to NO converter [*Ryerson et al.*, 2000] was used to measure NO and NO_2 in the effluent air from the flow reactor. The detection limit is better than 50 pptv for both NO and NO_2 for a 5-min averaging time. A 37% HONO to NO conversion efficiency was used to correct NO_2 data [*Ryerson et al.*, 2000].

3. Results and Discussion

[4] Results from a series of experiments confirmed that HNO_3 photolysis on Pyrex surface is a HONO source in the presence of moisture (Figure 1 and Table 2). Under the experimental conditions shown in Figure 1, the observed HONO production rate was in the range of $(1.0–1.5) \times 10^{-12}$ moles s^{-1} at a RH in the range of 20–80%. Based on the results of 8 separate experiments, the average HONO production rate normalized to the amount of adsorbed HNO_3 on surface, J_{HNO3_HONO}, is $(1.2 \pm 0.2) \times 10^{-5}$ s^{-1} under the irradiation equivalent to the noontime tropical sun

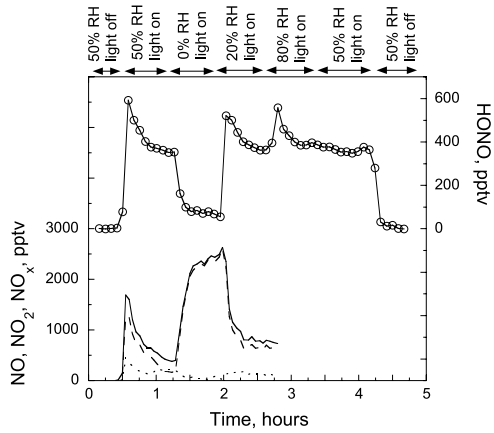

Figure 1. Concentrations of HONO (open circles with solid line), NO (dotted line), NO_2 (dashed line) and NO_x (solid line) in the effluent gas from a flow reactor during a photochemical experiment. The reactor surface was coated with 1.2×10^{-7} moles of HNO_3. The gas flow rate through the reactor was 3.5 L min^{-1}.

and at a RH of 50% and a temperature of 24°C (Table 2). In addition to HONO, a significant amount of NO_x, mainly in the form of NO_2, is produced by this process (Figure 1, Table 2), consistent with the recent field observations of light-induced NO_x emission from pine needle surfaces [*Hari et al.*, 2003] and from snowpack [*Honrath et al.*, 2000]. The overall production rate of (NO_x + HONO) normalized to the surface HNO_3, J_{HNO3_total}, increases from $(2.2 \pm 0.3) \times 10^{-5}$ s^{-1} (n = 3) at 50% RH to 6.0×10^{-5} s^{-1} at 0% RH.

[5] The observed J_{HNO3_total} values are about 2 orders of magnitude greater than the nitrate photolysis rate of $\sim 3 \times 10^{-7}$ s^{-1} in aqueous solutions [*Jankowski et al.*, 1999; *Mack and Bolton*, 1999] and the HNO_3 photolysis rate of about $\sim 7 \times 10^{-7}$ s^{-1} in the gas-phase [*Finlayson-Pitts and Pitts*, 2000]. The mechanism leading to this significant enhancement of the photolysis rate of HNO_3 on surfaces, compared to those in the homogeneous phases, is not clear. It may result from surface catalysis, as observed for various species such as N_2O_3 [*Sato et al.*, 2000], and N_2O [*Kato et al.*, 2000], an enhancement/red shift of its light absorption cross-section, and/or an increase in quantum yield. Further experiments are needed to understand the detailed mechanism. It is interesting to note that the production rates of both HONO and NO_x were significantly higher initially when the glass surface was exposed to light and rapidly decreased and stabilized with time. This suggests that the glass surface may not be uniform chemically and certain sites may be

Table 2. Normalized Production Rates of HONO (J_{HNO3_HONO}) and (HONO + NO_x) (J_{HNO3_total}) from HNO_3 Photolysis on Pyrex Surface[a]

RH, %	$J_{HNO3_HONO} \pm 1\sigma$, s^{-1}	$J_{HNO3_total} \pm 1\sigma$, s^{-1}
0	0.16×10^{-5} (n = 1)	6.0×10^{-5} (n = 1)
20	1.0×10^{-5} (n = 1)	2.8×10^{-5} (n = 1)
50	$(1.2 \pm 0.2) \times 10^{-5}$ (n = 8)	$(2.2 \pm 0.2) \times 10^{-5}$ (n = 3)
80	1.4×10^{-5} (n = 1)	ND[b]

[a]The n values in the parentheses are numbers of experiments. The values have been normalized to the amount of HNO_3 on the surface and to the full sun condition where aqueous nitrate photolysis rate is 3.0×10^{-7} s^{-1}. The temperature was 24 ± 2°C.
[b]ND, not determined.

19448007, 2003, 23, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2003GL018620, Wiley Online Library on [03/01/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

more active and effective in catalyzing HNO_3 photolysis than most sites. The rate constants presented here are derived from the stabilized signals.

[6] The production of HONO is found to be greatly enhanced by the presence of water, with the rate in dry air being about 1/10 that at 50% RH, despite much higher NO_x production under dry conditions (Figure 1). This suggests that NO_2 is the major primary product of HNO_3 photolysis on surfaces. The mechanism could proceed via (R1)–(R3), similar to that in aqueous nitrate photolysis [*Mack and Bolton*, 1999].

$$\text{(R1)} \qquad HNO_{3(ads)} + h\nu \rightarrow [HNO_3]^*_{(ads)}$$

$$\text{(R2)} \qquad [HNO_3]^*_{(ads)} \rightarrow HNO_{2(ads)} + O\left(^3P\right)_{(ads)}$$

$$\text{(R3)} \qquad [HNO_3]^*_{(ads)} \rightarrow NO_{2(ads)} + OH_{(ads)}$$

The $NO_{2(ads)}$ produced may further react with $H_2O_{(ads)}$ on surface under humid conditions, with its rate greatly enhanced by light [*Akimoto et al.*, 1987], to produce

$$\text{(R4)} \qquad HONO_{(ads)} : 2NO_{2(ads)} + H_2O_{(ads)} \rightarrow HONO_{(ads)} + HNO_{3(ads)}$$

The $HONO_{(ads)}$ produced may then desorb from the surface and be released into the gas phase. The actual mechanism of reaction (R4) may be more complex, as proposed by *Finlayson-Pitts et al.* [2003], and is beyond the scope of this study. Unlike the heterogeneous NO_2-H_2O reaction that is first-order toward water vapor concentration in the gas-phase [*Akimoto et al.*, 1987; *Finlayson-Pitts et al.*, 2003], the production yield of HONO from surface HNO_3 photolysis is almost independent of RH between 20% and 80%, although some moisture is necessary (Figure 1 and Table 2). This suggests that the photolysis of surface HNO_3 is the rate-limiting step in the overall process leading to HONO formation. This is supported by the linear relationship between HONO production rate and the amount of HNO_3 adsorbed on glass surface (Figure 2). This linear relationship was observed in the range of $(5–125) \times 10^{-8}$ moles m^{-2} at 50% relative humidity. The surface coverage by HNO_3 is well within a monolayer thickness of $\sim 1 \times 10^{-5}$ moles m^{-2} [*Masel*, 1996]. It should be pointed out that the actual surface HNO_3 photolysis rate may be higher than the observed J_{HNO3_total} values in Table 2, since two NO_2 molecules from (R3) are required to produce one HONO molecule, according to the reaction stoichiometry (R4).

[7] HNO_3 can be a major component of NO_y, particularly in regions far from industrial and urban pollution sources [*Finlayson-Pitts and Pitts*, 2000; *Buhr et al.*, 1990]. While HNO_3 dry deposition is considered to be a major sink for the oxidized nitrogen in the troposphere, some processes, such as NO + HNO_3 reaction on surface, can convert HNO_3 back to NO_x (''re-NOx-ification'') [*Mochida and Finlayson-Pitts*, 2000]. If the surface photochemistry of HNO_3 on Pyrex observed in our lab occurs in a similar fashion on other surfaces, such as leaves, rocks and soil, it can serve as a significant or even major re-NOx-ification pathway, especially in the low-NO_x regions. At a J_{HNO3_total} of $\sim 2.5 \times 10^{-5}$ s^{-1}, the photolysis lifetime of surface

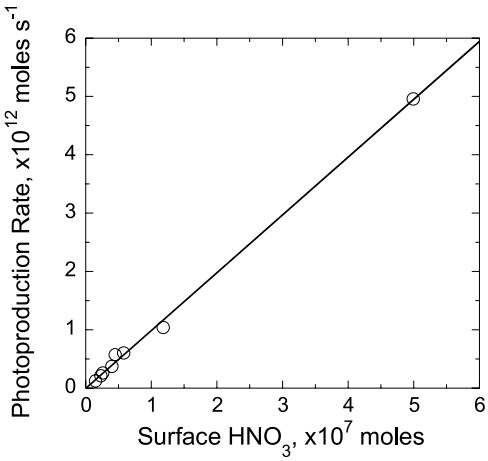

Figure 2. Relationship between photoproduction rate of HONO and the amount of adsorbed HNO_3 on the reactor surface at 50% RH. Line is the least-square fit ($r^2 = 0.99$).

HNO_3 is about 11 hours when exposed to full sun. During the summer, daily accumulative solar radiation is about 8–9 hours of noontime equivalent [*Finlayson-Pitts and Pitts*, 2000]. This means that a major fraction of the sunlight-exposed HNO_3 on ground surfaces would be recycled back to the overlying atmosphere as NO_x and HONO on a daily basis. More quantitatively, the upward flux (moles m^{-2} s^{-1}) of reactive oxidized nitrogen in the form of NO_x and HONO from HNO_3 photolysis on surfaces can be estimated by equation (1):

$$F_{up} = aJvCt \qquad (1)$$

where a is the fraction of deposited HNO_3 on surfaces exposed to full noontime sunlight with a photolysis rate of J (s^{-1}), v is the average HNO_3 dry deposition velocity (m s^{-1}), C is the ambient HNO_3 concentration (moles m^{-3}), and t is the accumulation time since the last precipitation event. Assuming that the surface HNO_3 is exposed to 1/4 of the full noontime sun during the day after 24 hours accumulation, with an average HNO_3 concentration of 700 pptv (3.1×10^{-8} moles m^{-3}) [*Thornberry et al.*, 2001] and an average dry deposition velocity of 2×10^{-2} m s^{-1}, the upward flux would be:

$$F_{up} = \tfrac{1}{4} \times 2.5 \times 10^{-5} \times 24 \times 3600 \times 2 \times 10^{-2} \times 3.1 \times 10^{-8}$$

$$\sim 3.3 \times 10^{-10} \text{ moles } m^{-2} \text{ } s^{-1} \left(\text{or } 1.2 \times 10^{-6} \text{ moles } m^{-2} \text{ } hr^{-1}\right).$$

It will result in a 30 pptv hr^{-1} increase in NO_x concentration in a 1-km well-mixed boundary layer, a very significant source for NO_x in rural environments. Furthermore, a significant fraction of this flux, e.g., about half at 50% RH, will be emitted as HONO. Since HONO is photochemically labile, its concentrations tend to be highest near the source, i.e., close to the ground. To simplify the calculation, if the produced HONO were assumed to be *uniformly* distributed within a near surface 100-m air column before being photolyzed, then the volume HONO production rate from surface HNO_3 photolysis would be $\sim$150 pptv hr^{-1}. At a measurement height of a few meters above the ground or

19448007, 2003, 23, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2003GL018620, Wiley Online Library on [03/01/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

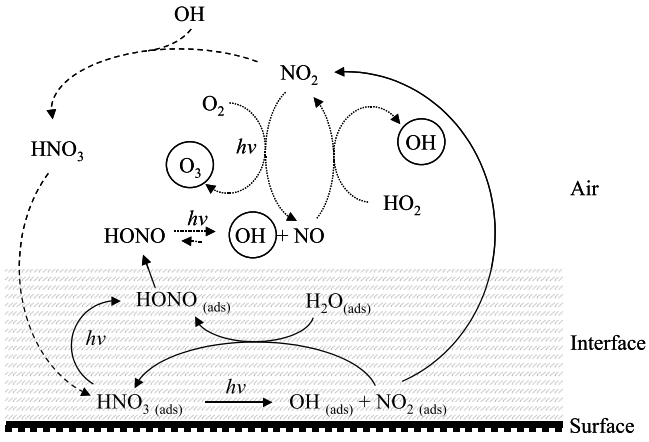

Figure 3. Effects of the photolytic remobilization of HNO_3 (''re-NOx-ification'') on ground surfaces on the chemistry of the overlying atmosphere. Solid arrows are processes responsible for surface HNO_3 remobilization, dashed arrows indicate removal of oxidized nitrogen from the atmosphere to ground surface by deposition, and dotted arrows are gas-phase reactions leading to formation of O_3 and OH radicals (in circles).

canopy surface, the HONO concentration should be higher than this assumed uniformly distributed value, and thus its volume production rate should be higher than this estimated value and closer to the observed HONO photolytic loss rate of 200–400 pptv hr^{-1} in the low-NO_x atmosphere (Table 1). This simple calculation lends further support to the hypothesis that HNO_3 photolysis is the major daytime HONO source in the low-NO_x rural atmospheric boundary layer [*Zhou et al.*, 2002a].

[8] Remobilization of HNO_3 via its photolysis on ground surfaces has significant atmospheric implications, especially in low-NO_x rural regions. This process would supply the overlying atmosphere with a new source of photochemically reactive nitrogen species, i.e., HONO and NO_x, and would thus significantly impact the chemistry of the remote low-NO_x atmospheric boundary layer by altering the radical pool, as illustrated in Figure 3. The recycling of HNO_3 deposited on ground surfaces back into photochemically reactive forms could be an important, or even the major, NO_x source in these environments, especially in the regions with high HNO_3/NO_x ratio and during dry periods. About half of the upward flux may be HONO when RH is greater than 20%, providing a significant OH source via its photolysis in the atmospheric boundary layer, as observed at several low-NO_x rural sites [*Zhou et al.*, 2002a]. With this new source of NO_x and HONO, the atmospheric boundary layer should be more reactive photochemically than we previously realized, leading to higher production of photooxidants, such as ozone and OH radicals.

[9] Our results from field and laboratory strongly suggest that atmospheric boundary layer models should take this surface process into consideration, especially for understanding the photochemistry in rural areas. To fully understand the importance of this process in surface layer atmospheric chemistry, more laboratory experiments are needed to study the catalytic effects on HNO_3 photolysis by more environmentally relevant surfaces, such as leaves, rocks and soil. In addition, to fully understand the significance of this surface process in different environments, such as forest and farm lands, HONO and NO_x flux measurements are necessary.

[10] **Acknowledgments.** This research is supported by the National Science Foundation (NSF) through grants ATM-9615748, ATM-0122708.

References

Akimoto, H., H. Takagi, and F. Sakamiki, Photoenhancement of the nitrous acid formation in the surface reaction on nitrogen dioxide and water vapor: Extra radical source in smog chamber experiments, *Int. J. Chem. Kinet.*, *19*, 539–551, 1987.

Buhr, M. P., D. D. Parrish, R. B. Norton, F. C. Fehsenfeld, R. E. Sievers, and J. M. Roberts, Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site, *J. Geophys. Res.*, *95*, 9809–9816, 1990.

Finlayson-Pitts, B. J., and J. N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic, San Diego, 2000.

Finlayson-Pitts, B. J., L. M. Wingen, A. L. Sumner, D. Syomin, and K. A. Ramazan, The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, *Phys. Chem. Chem. Phys.*, *5*, 223–242, 2003.

Hari, P., M. Raivonen, T. Vesala, J. W. Munger, K. Pilegaard, and M. Kulmala, Ultraviolet light and leaf emission of NO_x, *Nature*, *422*, 134, 2003.

Honrath, R. E., M. C. Peterson, M. P. Dziobak, J. E. Dibb, M. A. Arsenault, and S. A. Green, Release of NO_x from sunlight-irradiated midlatitude snow, *Geophys. Res. Lett.*, *27*, 2237–2240, 2000.

Huang, G., X. Zhou, G. Deng, H. Qiao, and K. Civerolo, Measurements of atmospheric nitrous acid, nitric acid and pernitric acid, *Atmos. Environ*, *36*, 2225–2235, 2002.

Jankowski, J. J., D. J. Kieber, and K. Mopper, Nitrate and nitrite ultraviolet actinometers, *Photochem. Photobiol.*, *70*, 319–328, 1999.

Kato, H., J. Lee, K. Sawabe, and Y. Matsumoto, Photochemistry of N_2O on Si(100): Surface photo-oxidation, *Surf. Sci.*, *445*, 209–223, 2000.

Kleinman, L., Y. N. Lee, S. R. Springston, J. H. Lee, L. Nunnermacker, J. Weinstein-Lloyd, X. Zhou, and L. Newman, Peroxy radical concentration and ozone formation rate at a rural site in southeastern United States, *J. Geophys. Res.*, *100*, 7263–7273, 1995.

Mack, J., and J. R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: A review, *J. Photochem. Photobiol. A: Chem.*, *128*, 1–13, 1999.

Masel, R. I., *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley, 1996.

Mochida, M., and B. J. Finlayson-Pitts, FTIR Studies of the Reaction of Gaseous NO with HNO_3 on Porous Glass: Implications for Conversion of HNO_3 to Photochemically Active NO_x in the Atmosphere, *J. Phys. Chem.*, *104*, 9705–9711, 2000.

Ryerson, T. B., E. J. Williams, and F. C. Fehsenfeld, An efficient photolysis sytem for fast-response NO_2 measurements, *J. Geophys. Res.*, *105*, 26,447–26,461, 2000.

Sato, S., D. Yamaguchi, T. Senga, and M. Kawasaki, Photodissociation Cross Sections of N_2O_3 Adsorbed on Au(111), *J. Phys. Chem. B*, *104*, 4863–4866, 2000.

Thornberry, et al., Observations of reactive oxidized nitrogen and speciation of NO_y during the PROPHET summer 1998 intensive, *J. Geophys. Res.*, *106*, 24,359–24,386, 2001.

Zhou, X., H. J. Beine, R. E. Honrath, J. D. Fuentes, W. Simpson, P. B. Shepson, and J. Bottenheim, Snowpack photochemical production as a source for HONO in the Arctic boundary layer in springtime, *Geophys. Res. Lett*, *28*, 4087–4090, 2001.

Zhou, X., K. Civerolo, H. Dai, G. Huang, J. Schwab, and K. Demerjian, Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State, *J. Geophys. Res.*, *107*, doi:10.1029/2001JD001539, 2002a.

Zhou, X., Y. He, G. Huang, T. D. Thornberry, M. A. Carroll, and S. B. Bertman, Photochemical Production of HONO on Glass Sample Manifold Wall Surface, *Geophys. Res. Lett*, *29*, doi:10.1029/2002GL015080, 2002b.

S. Bertman, Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA.

K. Civerolo, New York State Department of Environmental Conservation, 625 Broadway, Albany, NY 12233-3259, USA.

J. Schwab, Atmospheric Sciences Research Center, State University of New York at Albany, Albany, NY 12203, USA.

X. Zhou, H. Gao, Y. He, and G. Huang, Wadsworth Center, New York State Department of Health, and School of Public Health, State University of New York at Albany, Albany, NY 12201-0509, USA. (zhoux@wadsworth.org)

19448007, 2003, 23, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2003GL018620, Wiley Online Library on [03/01/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License